

## Catalysts for Autothermal Reforming

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### Objectives

- Develop advanced autothermal reforming (ATR) catalysts that meet DOE targets for fuel-flexible fuel processors, i.e., fuel efficiency  $\geq 99.9\%$ ,  $H_2$  selectivity  $\geq 80\%$ , gas-hourly space velocity (GHSV)  $\geq 200,000\text{ h}^{-1}$ , durability  $\geq 5000\text{ h}$ , and cost  $\leq \$5/\text{kWe}$ .
- Develop a better understanding of reaction mechanisms to increase catalytic activity, reduce deactivation, and improve sulfur tolerance.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cell section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Start-up/Transient Operation
- J. Durability
- K. Emissions and Environmental Issues
- N. Cost

### Approach

- Building on past experience, we are investigating two classes of materials, transition metals supported on mixed-oxide substrates and perovskites containing no precious metals.
- Determine catalyst performance (i.e., yields of  $H_2$ , CO,  $CO_2$ , and  $CH_4$ ) as a function of catalyst formulation, fuel composition (including sulfur content), and operating parameters (e.g.,  $O_2:C$  and  $H_2O:C$  ratios, temperature, and GHSV).
- Conduct catalyst characterization and mechanistic studies to gain insight into reaction pathways.
- Work with catalyst manufacturers to optimize catalyst structure and performance.

### Accomplishments

For transition metals on mixed oxide supports

- Optimized catalyst formulation to improve performance of monoliths.
- Demonstrated 54.6 vol%  $H_2$  (dry,  $N_2$ -free) from sulfur-free ( $<450\text{ ppb S}$ ) gasoline at GHSV of 110,000  $\text{h}^{-1}$  with Rh catalyst on a monolith.
- Identified Pt sintering as a major cause for catalyst deactivation.
- Identified oxide formulation that does not lose surface area during reforming.

For the Ni-based perovskites

- Identified  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$  as a composition with improved structural stability compared to  $\text{LaNiO}_3$  under ATR conditions.
- Demonstrated <50% loss in activity with benchmark fuel with 50 ppm S.

### Future Directions

- Evaluate catalyst performance on a larger scale using 1-5 kWe adiabatic reactors to confirm microreactor results, better evaluate long-term and startup performance, and determine optimal geometry for structured support.
- Work to decrease precious metal loading while improving catalyst stability and sulfur tolerance.
- Work to improve catalyst activity and sulfur tolerance of perovskite catalysts.
- Address the effect of rapid startup on catalyst stability.
- Increase our fundamental understanding of reaction processes and mechanisms for deactivation and sulfur poisoning.

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## Introduction

Catalytic autothermal reforming (ATR) of hydrocarbon fuels to generate  $\text{H}_2$  has been widely accepted as the most promising route to meet the efficiency, weight and volume, durability, and cost goals for on-board fuel processors for automotive fuel cell systems. Argonne National Laboratory is developing new reforming catalysts tailored to meet the unique operating requirements for reforming complex fuel mixtures, such as gasoline. Two different classes of materials are being examined: Group VIII transition metals (e.g., platinum, rhodium, or nickel) supported on an oxide ion-conducting substrate (e.g., gadolinium-doped ceria (CGO)), and mixed non-noble metal oxides with the  $\text{ABO}_3$  stoichiometry and the perovskite structure. The transition metal-based catalysts have demonstrated near-equilibrium yields of  $\text{H}_2$  from a number of fuels, including gasoline, diesel, and natural gas, exhibiting high catalytic activity and resistance to coking. Süd-Chemie, Inc., of Louisville, Kentucky, currently produces this catalyst under a licensing agreement.

## Approach

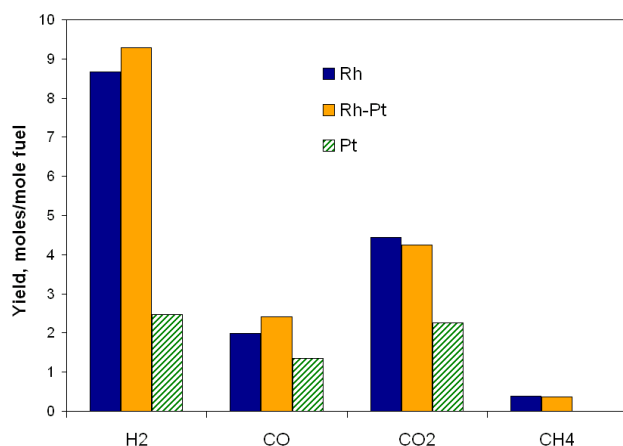
Catalyst samples as powders and coated on monoliths are evaluated for  $\text{H}_2$  yield, fuel conversion, and resistance to coking and sulfur poisoning as a function of operating parameters (such

as the type of fuel, its sulfur content,  $\text{O}_2:\text{C}$  and  $\text{H}_2\text{O}:\text{C}$  ratios, and reaction temperature) in a microreactor system. Fuels tested include sulfur free (<450 ppb S) and low sulfur (~30 ppm S) gasolines, isooctane (2,2,4-trimethylpentane), and a benchmark fuel mixture<sup>1</sup>. Catalyst characterization techniques such as extended X-ray absorption fine structure spectroscopy (EXAFS) are used to understand changes in catalyst morphology during ATR and to help improve catalyst performance and stability.

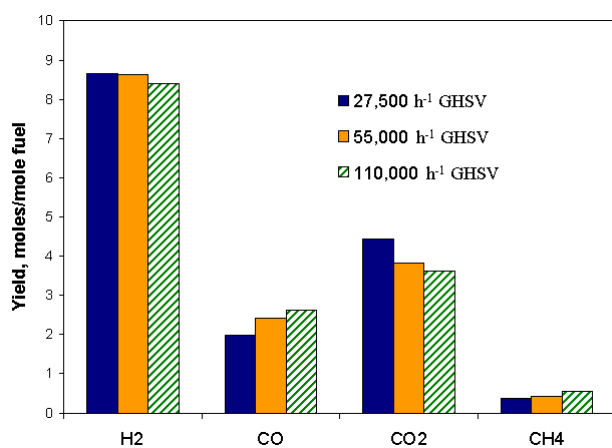
## Results

**Transition Metals Supported on an Oxide-Ion Conducting Substrate.** Monoliths coated with Rh-containing catalysts, Rh-CGO or Rh-Pt-CGO, produced reformates from sulfur-free gasoline with a higher  $\text{H}_2$  yield, 8.7 and 9.3 moles of  $\text{H}_2$  per mole of gasoline, respectively, than the monolith coated with a catalyst containing only Pt (2.5 moles of  $\text{H}_2$  per mole of gasoline) as shown in Figure 1. The methane yield was 0.4 moles of  $\text{CH}_4$  per mole of gasoline for both Rh-CGO and Rh-Pt-CGO. Non-methane hydrocarbons included  $\text{C}_2\text{-C}_6$  paraffins and the aromatics benzene, toluene, and xylenes. For Rh-CGO, the  $\text{H}_2$  yield increased to 9.3 moles of  $\text{H}_2$  per mole of fuel when the reaction temperature was increased from 700 to 750°C. For Pt-CGO, the  $\text{H}_2$  yield increased from 2.5 to 8.4 moles of  $\text{H}_2$  per mole of gasoline as the reaction temperature was increased from 700 to 800°C. For ATR, the steam reforming

component of the reaction produces the  $H_2$ , and the higher  $H_2$  yields observed with the Rh-containing catalysts are consistent with various studies which have shown that Rh is the most active Group VIII transition metal for steam reforming.<sup>2</sup> As the GHSV was increased from 27,500 to 110,000  $h^{-1}$ , the  $H_2$  yield decreased slightly from 8.7 to 8.4 moles of  $H_2$  per mole of gasoline for Rh-CGO as shown in Figure 2. On a concentration basis, the  $H_2$  concentration decreased from 55.4 to 54.6 vol% (dry,  $N_2$ -free) as the GHSV was increased from 27,500 to 110,000  $h^{-1}$ . Tests are in progress to determine if modifying the structured support can reduce hydrocarbon breakthrough.



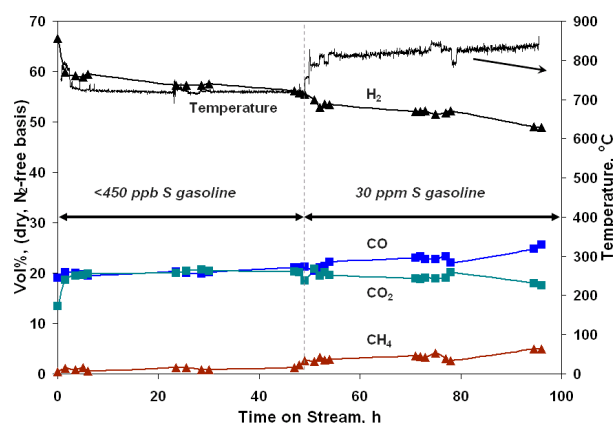
**Figure 1.** Comparison of the  $H_2$ , CO,  $CO_2$ , and  $CH_4$  Yields Produced from <450 ppb S Gasoline Catalyzed by Rh-, Rh-Pt, or Pt-CGO at 700°C



**Figure 2.** Effect of GHSV on  $H_2$ , CO,  $CO_2$ , and  $CH_4$  Yields Produced from <450 ppb S Gasoline Catalyzed by Rh-CGO at 700°C

Previous studies have shown that Pt-CGO is more sulfur tolerant than Rh-CGO.<sup>1</sup> The sulfur tolerance of Rh-Pt-CGO was evaluated by reforming two gasolines, one which contained <450 ppb S and the other which contained 30 ppm S. As shown in Figure 3, the  $H_2$  concentration decreased from 58.2 to 54.8 vol%, representing a 6% decrease, during the first 48 h with sulfur-free gasoline. The fuel was then switched to the 30 ppm S gasoline. The  $H_2$  concentration decreased further to 49.8 vol%, which represents a 10% decrease, over the next 48 h, indicating that sulfur in the fuel was poisoning the catalyst. EXAFS analyses showed that Pt is highly dispersed on Pt-CGO before ATR but undergoes sintering during ATR. Sulfur in the fuel appears to enhance the sintering of Pt. Similar studies are in progress for the Rh and Rh-Pt.

**Mixed Metal Oxides with the Perovskite Structure.** We have previously reported that for the lanthana-based perovskites containing first-row transition metals (i.e.,  $LaCrO_3$ ,  $LaMnO_3$ ,  $LaFeO_3$ ,  $LaCoO_3$ , and  $LaNiO_3$ ), the highest  $H_2$  yields are observed with the least stable complexes,  $LaCoO_3$  and  $LaNiO_3$ , which decompose into  $La_2O_3$  and metallic Co and Ni, respectively, under ATR conditions.<sup>3</sup> The stability of  $LaNiO_3$  under ATR was increased by replacing some of the Ni with Cr, termed “B-site” doping. This resulted in a slight decrease in the  $H_2$  yield, which could be recovered



**Figure 3.** Comparison of vol% of  $H_2$ , CO,  $CO_2$ ,  $CH_4$ , and Total Hydrocarbons (HCs) in Reformate Produced from <450 ppb S and 30 ppm S Gasolines Catalyzed by Rh-Pt-CGO/Monolith

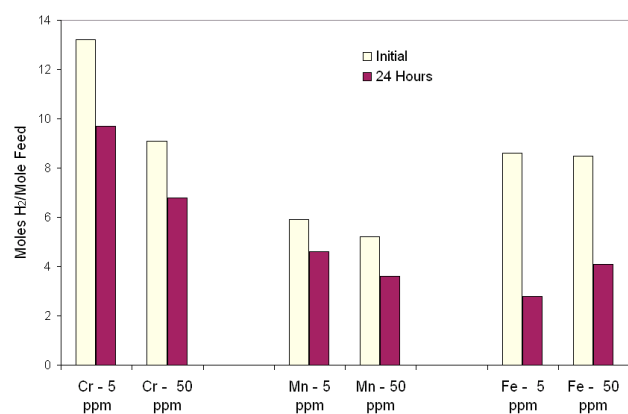
by replacing some of the La with Sr, termed "A-site" doping.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$  was identified as the optimal composition.

The sulfur tolerance of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$  was evaluated by comparing the  $\text{H}_2$  yield from reforming benchmark fuel containing two different S contents, 5 and 50 ppm, added as benzothiophene.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$  is susceptible to sulfur poisoning with the decrease in the  $\text{H}_2$  yield being greater and more rapid at the higher sulfur content. Attempts to improve the sulfur tolerance by replacing Cr with metals such as Mn or Fe were not successful, as shown in Figure 4.

## Conclusions

### Transition Metal(s) Supported on an Oxide-Ion Conducting Substrate

- Showed that formulations containing Rh are the best-performing ATR catalysts.
- Demonstrated that Rh-CGO on a monolith can produce a reformat containing 54.6 vol%  $\text{H}_2$  (dry,  $\text{N}_2$ -free) from a <450 ppb S gasoline at a GHSV of 110,000  $\text{h}^{-1}$ .
- Using EXAFS, showed that Pt sinters under ATR conditions and that S may enhance sintering.



**Figure 4.** Comparison of the Effect of 5 and 50 ppm S on  $\text{H}_2$  Yield Produced from Benchmark Fuel Catalyzed by  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$ ,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ , and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.9}\text{Ni}_{0.1}\text{O}_3$

### Mixed Metal Oxides with the Perovskite Structure

- Identified  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3$  as a composition with improved structural stability compared to  $\text{LaNiO}_3$  under ATR conditions.
- Determined that deactivation due to sulfur poisoning depends on the sulfur content in the fuel; however, complete loss of activity was not observed.

## References

1. J. P. Kopasz, D. Applegate, X. Wang, L. Miller, S. Ahmed and M. Krumpelt, "Effects of Fuels and Contaminants on Performance of Reforming Catalysts," 2001 Annual Progress Report, Fuels for Advanced CIDI Engines and Fuel Cells, U.S. Department of Energy, Office of Transportation Technologies, Washington, D.C.
2. D. L. Trimm, Z. I. Onsan, Catal. Rev. Sci. Eng. 2001, 43(1-2), 31.
3. T. Krause, J. Mawdsley, C. Rossignol, J. Kopasz, D. Applegate, M. Ferrandon, J. D. Carter, and M. Krumpelt, "Catalytic Autothermal Reforming," FY2002 Progress Report for Hydrogen, Fuel Cells, and Infrastructure Technologies Program, U.S. Department of Energy, Office of Hydrogen, Fuel Cells, and Infrastructure Technologies, Washington, D.C.

## FY 2003 Publications/Presentations

### Publications

1. M. Krumpelt, T. R. Krause, J. D. Carter, J. P. Kopasz, and S. Ahmed, "Fuel Processing for Fuel Cell Systems in Transportation and Portable Power Applications," Catalysis Today, 77, (1-2), 3-16 (2002).
2. M. G. Sobacchi, A. V. Saveliev, A. A. Fridman, L. A. Kennedy, S. Ahmed, and T. Krause, "Experimental Assessment Of A Combined Plasma/Catalytic System For Hydrogen Production Via Partial Oxidation Of Hydrocarbon Fuels," Int. J. Hydrogen Energy, 27, 635-642 (2002).

**Presentations**

1. Theodore Krause, Magali Ferrandon, Cécile Rossignol, "Reforming Catalysts For On-Board Fuel Processing," To be presented at the 226th American Chemical Society National Meeting, New York, NY, September 7-11, 2003.
2. Theodore Krause, Cécile Rossignol, Magali Ferrandon, John Kopasz, Jennifer Mawdsley, Joong-Myeon Bae, "Transition Metals on Oxide Ion Conducting Supports as Reforming Catalysts for Fuel Cell Systems," Presented at the 18th Annual Meeting of the North American Catalysis Society, Cancun, Mexico, June 1-6, 2003.
3. J. R. Mawdsley, T. R. Krause and J. P. Kopasz, "Perovskite Catalysts for Producing Hydrogen Using Gasoline Fuel," Presented at the 2003 American Ceramic Society Annual Meeting, Nashville, TN, April 28-30, 2003.
4. Theodore Krause, Cécile Rossignol, Magali Ferrandon, John Kopasz, and Joong-Mayeon Bae, "Pt And Rh Supported On Oxide-Ion Conducting Substrates As Catalysts For Generating H<sub>2</sub> For Fuel Cells," Presented at the 2003 Spring National Meeting of the American Institute of Chemical Engineers, New Orleans, LA, March 30-April 3, 2003.